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THE SEPARATION OF PIPERYLENE CONCENTRATE BY EXTRACTIVE DISTILLATION

BY

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B.S., Florida Institute of Technology, 1978

RESEARCH REPORT

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ABSTRACT

Piperylene concentrate, the five-carbon olefin and diolefin by-product of ethylene production, is being produced in increasing quantities as liquid feedstocks become more prevalent. At present, the concentrate is used primarily in resin production for the adhesives industry. Since this use is economically unattractive, a separation of the concentrate into pure compounds is industrially desirable.

The evaluation of the effectiveness of several solvents for extractive distillation of piperylene concentrate was performed. This study resulted in the selection of acetonitrile as the most effective and most economical solvent investigated. Various distillation conditions were studied and optimization was based on these results.

ACKNOWLEDGEMENTS

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The author would also like to thank Dr. Guy Mattson, Department of Chemistry Chairman, and the Department Faculty and Staff for their friendship and encouragement during the execution of this study.

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INTRODUCTION

Ethylene, the petrochemical which ranks first in total market value and second in metric tons produced worldwide with over nine billion tons produced in the United States alone in 1975[1], has been produced from a variety of feedstocks ranging from ethane to naphtha to gas oils. Because of their composition, cracking processes using gaseous feedstocks result in near complete conversion to ethylene; with heavier feeds more by-products are formed. For example, based on a once-through pyrolysis, the percent yields of ethylene are 50.5% for ethane feed and 32.3% for light naphtha feed. The corresponding five-carbon by-product yields are 0.22% and 3.85% for ethane and light naphtha feeds respectively[1]. A present Dow Chemical Company process produces a 24.4% yield of ethylene and a 1.6% yield of five carbon by-product based on cracking residual fuel oil[2]. As ethylene production moves to heavier feedstocks, which is the current trend in the United States,[2] more of the by-products are produced and their separation and utilization have become of economic interest to ethylene producers. It has been predicted that by 1982-1983 an estimated 50% of all United States ethylene production will be coming from naphtha and gas oils.

The by-product with which this project deals is the five-car-

bon mixture of olefins and diolefins obtained by fractionation of a product stream from the Dow Chemical Company's gas oil cracking process. Since 1,3-pentadiene, known commonly as piperylene, is the major component of this by-product stream, the mixture is called "piperylene concentrate". A typical composition of piperylene concentrate is given in Table I.

The amount of piperylene concentrate produced depends not only on the feed employed but also on the cracking conditions. In general, the more severe the cracking conditions are, the more diene is produced[3]. At present, piperylene concentrate is used to produce resins which are ultimately used as tackifiers for various adhesives.

The diene content of petroleum fractions has been used as a component of petroleum resins used in the paint and plastics industries. These resins are made by polymerizing the unsaturated content with ionic catalysts[3].

At present, two resins being produced from 1,3-pentadiene are Quintone® and Quintol®, manufactured by K. J. Quinn and Company, Inc., Malden, MA. Quintone® is a resin used as a tackifier for pressure-sensitive adhesives, hot melt adhesives, and in rubber compounding. Quintol®, a liquid polymer, resembles linseed oil and may be used in paints, coatings, sealants, and caulking compounds because of its quick-drying properties[4].

A Diels-Alder reaction of 1,3-pentadiene with maleic anhydride produces a commercial epoxy hardener. Acids and esters of

TABLE I

COMPOSITION OF PIPERYLENE CONCENTRATE

COMPOUND	PERCENT BY WEIGHT
trans-1,3-Pentadiene	33.9
Cyclopentene	27.8
cis-1,3-Pentadiene	20.4
2-Methyl-2-butene	10.2
1,3-Cyclopentadiene	0.8
2-Methyl-1,3-butadiene	0.5
Remainder[a]	6.4

[a]Remainder consists of trace amounts of pentane, 2,2-dimethylbutane, cyclopentadiene, and other unidentified hydrocarbons.

this adduct may be used as plasticizers and softening agents for resins, gums, and lacquer films[5]. Excess amounts of piperylene are used as fuel for combustion furnaces and as a gasoline blend feedstock, uses which are less economically desirable than the resin uses.

Both cis- and trans-1,3-pentadiene have been reported to have been polymerized individually and with styrene as a comonomer[6]. Coordination catalysts have been used to produce trans-polypiperylene[7].

Cyclopentene has already found a place in the polymer industry. The vulcanized polymer has properties similar to polybutadiene and natural rubber. This vulcanized polymer has been examined as a potential tire elastomer because of high tensile strength, resistance to aging, retention of physical properties after exposure to heat, and resistance to crack formation on exposure to ozone. Another polymer of cyclopentene has properties similar to 80% cis-polybutadiene. Desirable properties of this amorphous polymer include excellent low-temperature flexibility due to its low glass-transition temperature[8].

Cyclopentene has been copolymerized with the reaction product of 1,5-cyclooctadiene and hexachlorocyclopentadiene to form a compound which exhibits good flame resistance to swelling by oils. Polymers of cyclopentene have been hydrogenated to form compounds which resemble a linear polyethylene.[8]

One obstacle in developing economically attractive uses for piperylene concentrate lies in the fact that the concentrate is a mixture of several components. In order to develop additional potential uses for the individual compounds it is first necessary to separate them into a purer form. This has been the objective of this project, with emphasis on obtaining pure cyclopentene.

Due to the similarity in boiling points of the components in piperylene concentrate (Table II), separation by simple fractionation is impossible. Other methods, including the use of molecular sieves have been either unsuccessful or uneconomical. The results presented in this report, obtained by extractive distillation, indicate a feasible method for separation of piperylene concentrate into three fractions: 2-methyl-2-butene, cyclopentene, and cis- and trans-1,3-pentadiene.

TABLE II

BOILING POINTS OF COMPONENTS IN PIPERYLENE CONCENTRATE

COMPOUND	BOILING POINT (°C)	REFERENCE NUMBER
2-Methyl-1,3-butadiene	34.1	9
2-Methyl-2-butene	38.6	9
trans-1,3-Pentadiene	42.0	9
1,3-Cyclopentadiene	42.5	3
Cyclopentene	44.3	9
cis-1,3-Pentadiene	44.9	9

EXPERIMENTAL

Analysis

A Perkin-Elmer Sigma I Gas Chromatographic System with a flame ionization detector was employed for quantitative analysis of starting materials and products. This system automatically computed the percent by weight of each component in the sample by using the total integrated peak area, the area under the individual peaks, and a component response factor. Since the molecular weights of all components in piperylene concentrate are similar (68 ± 2 a.m.u.), response factors of 1.00 were used for all components[10].

The column used for analysis of the components in piperylene concentrate consisted of a ten foot length of one-eighth inch diameter stainless steel tubing packed with 20 weight percent sebaconitrile (Pfaltz and Bauer, Inc.) on 80-90 mesh acid washed Anakrom C22 (Analabs, Inc.), followed by a 20 foot length of one-eighth inch diameter stainless steel tubing packed with 15 weight percent bis(2-methoxyethyl) adipate (Supelco, Inc.) on 60-80 mesh non-acid washed Chromsorb W (Analabs, Inc.). This column was conditioned for ten hours at 100°C with a helium flow of 25 ml per minute prior to use.

After continued use, this column tended to become contami-

nated with solvent and the heavy materials present in piperylene concentrate, causing retention times to decrease. In order to maintain consistent retention times for identified components, reconditioning was accomplished at 100°C with helium flow of 10 ml per minute for ten to twelve hours or, with helium flow of 25 ml per minute for one hour.

Both starting materials and products were analyzed isothermally at 60°C with a helium flow of 25 ml per minute. The injector was heated to 75°C and the flame ionization detector operated at 250°C. Under these conditions, all major components were eluted within 22 minutes (see Table III). None of the solvents investigated eluted from the column under these conditions. Some minor components in piperylene concentrate were identified by analyzing a series of standards under these same conditions (Table IV).

Analyses performed using this method had a relative standard deviation (95% confidence level) of 1.4% for 2-methyl-2-butene, 0.38% for cyclopentene, 0.66% for trans-1,3-pentadiene, and 1.3% for cis-1,3-pentadiene.

It was found that the retention times of 1-pentene and 2-methyl-2-butene on the above column coincided. In order to resolve these components a six foot length of one-eighth inch stainless steel tubing packed with 60-80 mesh molecular sieves Type 5A (Perkin-Elmer) was used. An isothermal analysis at 120°C with a helium flow of 20 ml per minute was used. The injector was heated

TABLE III

RETENTION TIME, IDENTITY, AND CONCENTRATION OF COMPONENTS IN PIPERYLENE CONCENTRATE

PEAK NUMBER	RETENTION TIME (MINUTES)[a]	IDENTITY	PERCENT BY WEIGHT
1	6.74	Pentane	trace
2	7.99	2,2-Dimethylbutane	trace
3	8.75	———	1.3
4	9.35	———	2.0
5	10.03	2-Methyl-2-butene	10.2
6	11.29	———	2.0
7	11.70	———	0.9
8	12.43	———	0.2
9	13.28	2-Methyl-1,3-butadiene	0.5
10	14.18	Cyclopentene	27.8
11	15.98	trans-1,3-Pentadiene	33.9
12	17.29	cis-1,3-Pentadiene	20.4
13	20.03	1,3-Cyclopentadiene	0.8

[a]Retention Time decreases as column ages.

TABLE IV

RETENTION TIME AND IDENTITY OF STANDARDS

PEAK NUMBER	RETENTION TIME (MINUTES)[a]	IDENTITY	SUPPLIER
1	6.74	Pentane	J. T. Baker
2	7.99	2,2-Dimethylbutane	Supelco
3	8.63	2-Methyl-1-butene	Pfaltz & Bauer
4	9.46	2-Methylpentane	Supelco
5	9.65	2,3-Dimethylbutane	Supelco
6	10.01	1-Pentene	Pfaltz & Bauer
7	10.03	2-Methyl-2-butene	Pfaltz & Bauer
8	10.56	3-Methylpentane	Supelco
9	11.37	4-Methyl-1-pentene	Supelco
10	11.39	Hexane	Burdick & Jackson
11	11.73	Cyclopentane	J. T. Baker
12	11.76	4-Methyl-2-pentene	Supelco
13	13.17	2,4-Dimethylpentane	Supelco
14	13.28	2-Methyl-1,3-butadiene	Aldrich
15	14.18	Cyclopentene	J. T. Baker
16	14.42	1-Hexene	Supelco
17	14.68	2-Methyl-1-pentene	Supelco
18	15.23	trans-2-Hexene	Supelco
19	15.84	2-Ethyl-1-butene	Supelco
20	15.98	trans-1,3-Pentadiene	Aldrich
21	16.84	cis-2-Hexene	Supelco
22	17.29	cis-1,3-Pentadiene	Reference 11
23	18.58	3-Methylhexane	Supelco
24	18.69	2,3-Dimethylpentane	Supelco
25	20.03	1,3-Cyclopentadiene	Reference 11
26	21.61	Cyclohexane	Mallinckrodt

[a]Retention time decreases as column ages.

to 75°C and the flame ionization detector operated at 250°C.

Retention times of additional standard compounds also coincided on the sebaconitrile-bis(2-methoxyethyl) adipate column (see Table III) but were not resolved for two reasons. First, they may not have been present in piperylene concentrate; or second, if one of the pair was present, the concentration was very low.

The presence of acetonitrile in the overhead product was qualitatively determined by infrared analysis. Spectra of pure acetonitrile (Burdick and Jackson Laboratories, Inc.), piperylene concentrate (undistilled), and overhead product fractions were obtained. Piperylene concentrate showed no absorption at 2300 and 2250 cm^{-1}, the characteristic absorptions of the nitrile functional group. This absorption was small but definite in the overhead product samples. Solvent presence was quantified by gas chromatography.

A Perkin-Elmer Sigma I System was again used with a flame ionization detector. The column was a six foot length of one-eighth inch diameter copper tubing packed with 50 weight percent 100-120 mesh Porapak Q (Waters Associates, Inc.) and 50 weight percent 100-120 mesh Porapak QS (Waters Associates, Inc.). This column was conditioned at 180°C with a helium flow of 10 ml per minute for 48 hours prior to use.

Although the Porapak column failed to separate the components of piperylene concentrate from one another, it did effect a sepa-

ration of acetonitrile from all piperylene components. The analysis was temperature programmed starting at 100°C for five minutes, then rising to 150°C at 10°C per minute. This temperature was held until all components were eluted, about 20 minutes. Helium flow was 25 ml per minute; the injector was heated to 100°C and the flame ionization detector operated at 250°C.

Apparatus

A 500-ml three-necked round-bottomed flask was used as the still pot. One side neck was used for an oil-filled thermocouple well while the other contained a needle with a sampling port. The center neck was connected to the bottom of the distillation column. For initial solvent screening a glass wool insulated 40-cm sieve tray column containing 11 physical plates and eight theoretical plates was used. After establishing that acetonitrile was the most effective solvent screened, the small column was replaced with a 76-cm vacuum jacketed sieve tray column that contained 21 physical and 12 theoretical plates. Both sieve tray columns had 2.4-cm (diameter) trays spaced 2.8 cm apart.

The top of the distillation column was fitted with a 23-cm feed section through which solvent was pumped from a hot water bath during continuous runs. Solvent flow was monitored by passing the solvent through a flow meter prior to introduction to the column. A heating tape was wrapped around the Teflon® solvent lines to

maintain the desired solvent temperature. A thermocouple was attached to the solvent feed line to monitor solvent feed temperature. Above the solvent feed section was located a 30-cm liquid-dividing still head which was operated by an automatic reflux ratio device. An oil well was located in the still head and contained a thermocouple used to monitor head temperature. Overhead product was withdrawn by means of a receiver assembly and collected in a receiving flask immersed in an ice-water bath. Vapors were condensed above the still head in a 30-cm Friedrichs condenser through which refrigerated isopropanol was circulated.

Distillation Procedure

The applicable apparatus as described was assembled by lightly greasing all ground glass joints and clamping connections. All exposed (non-vacuum jacketed) portions of the apparatus were wrapped with glass wool. The pot was charged with predetermined volumes of piperylene concentrate and solvent for batch operation, or with piperylene concentrate only for continuous operation. The flask was attached to the column and a two-piece heating mantle was placed around the flask. A variable voltage supply was used to provide power to heat the bottom portion of the mantle while the top portion was not heated. Temperatures of the pot, head, and solvent feed (for continuous operation) were monitored throughout each determination by thermocouples attached to a dig-

ital readout.

When all connections were made and exposed parts of the apparatus were insulated, heat was applied to the still pot contents and cooled isopropanol was introduced into the condenser. In continuous operation the solvent feed was started when the pot contents began to boil. Lag time for solvent travel from the inlet to the bottom plate was neglible (less than one minute).

When the head temperature rose to approximately 40°C, total reflux was established and allowed to continue with no product withdrawal for 30 to 45 minutes to establish equilibrium. An initial 0.5 to 1.0 ml portion of overhead product was discarded and the next 0.5 ml was taken as the first head sample. Immediately following each head sample collection, a 0.25 ml pot sample was withdrawn through the pot sampling needle by attaching a syringe to the needle, withdrawing the sample, and detaching the syringe to place the sample in a vial. All samples were placed in prelabeled vials and immediately capped and placed in an ice-water bath or refrigerated until analyzed by gas chromatography.

At the completion of each distillation, the apparatus was cooled, the flask removed and its contents measured, and the flask and fittings thoroughly cleaned. The column and head sections of the apparatus were cleaned by pouring about 150 ml of acetone into the condenser in 25 ml aliquots with the reflux ratio device on and collecting the cleansing solution at the bottom of the column

and at the receiver.

When acetonitrile solvent was discovered to be present in the overhead product, it was found to have resulted from entrainment in the vapors traveling up the column. This was shown by placing the 40-cm column between the feed section and the head section. Overhead products obtained from continuous distillation with this apparatus contained no solvent. Separation of solvent (acetonitrile) from piperylene concentrate can be achieved by simple fractionation.

Operating hold-up for each column was determined by quickly removing the distillation flask during operation and collecting the liquid which drained from the hot column[12]. The 40-cm column was determined to have an operating hold-up of 5 ml; the 76-cm column hold-up was 17 ml.

Static hold-up was determined by adding a measured quantity of liquid into the condenser and collecting and measuring that which readily flows through. Static hold-up was then determined by the difference between that which was introduced and that which was collected[12]. Static hold-up for the 40-cm column was 2 ml while that for the 76-cm column was 10 ml.

Total column hold-ups, i.e. the sum of operating and static hold-ups, were found to be 7 ml for the 40-cm column and 27 ml for the 76-cm column.

Determination of Theoretical Plates

The theoretical plate determinations for the two sieve tray columns were performed using the McCabe-Thiele graphical method[12] and a mixture of benzene (Mallinckrodt) and carbon tetrachloride (Mallinckrodt). Known amounts of benzene and carbon tetrachloride were weighed into the still pot. The pot was connected to the column with the feed section and still head in place. The mixture was heated until total reflux was attained and total reflux continued for 35 minutes to establish column equilibrium. The reflux ratio device was then engaged to withdraw a head sample while at the same time a pot sample was taken; these samples were cooled in ice. The concentrations of the respective samples were determined by measuring their refractive indices at 20°C and then comparing them to a previously prepared calibration curve.

Vapor-liquid equilibrium data[12] for the benzene-carbon tetrachloride system were plotted as mole percent carbon tetrachloride present in the vapor phase versus mole percent carbon tetrachloride in the corresponding equilibrium liquid phase. A 45° line was drawn on the same plot as the vapor-liquid equilibrium curve.

The liquid concentration in the pot sample was found on the horizontal axis and a line drawn vertically from the point to intersect the equilibrium line. The second necessary point was found by locating the head sample concentration on the horizontal axis and drawing a vertical line from that point to the point on

the 45° line corresponding to the same concentration. Stepwise construction of horizontal and vertical lines between the equilibrium line and the 45° line (steps) from the pot sample concentration to the head sample concentration gave the number of theoretical plates required to produce the difference in concentration between the pot and head sample concentrations.

Determination of Relative Volatilites

The relative volatility of two components; i and j, in a mixture is defined as

$$\alpha_{ij} = \frac{\gamma_i}{\gamma_j} \cdot \frac{P_i^\circ}{P_j^\circ} = S_{ij} \frac{P_i^\circ}{P_j^\circ}$$

where α_{ij} is the relative volatility of i (light component) to j (heavy component); P_i° and P_j° correspond to the saturated vapor pressures of pure components i and j respectively; and γ_i and γ_j are defined as the thermodynamic activity coefficients of components i and j respectively. S_{ij} is the selectivity of a solvent used in extractive distillation and is a function of the solvent and the conditions of the distillation.

Normal relative volatilities of the four major components found in piperylene concentrate (Table V) were calculated using their normal boiling points at 1 atm (Table II), along with generalized vapor pressure charts for hydrocarbons given in Reference 13.

TABLE V

RELATIVE VOLATILITIES OF MAJOR COMPONENTS IN PIPERYLENE CONCENTRATE WITH RESPECT TO CYCLOPENTENE AT 40°C

COMPOUND	NORMAL	IN THE PRESENCE OF ACETONITRILE
2-Methyl-2-butene	1.20	1.25
trans-1,3-Pentadiene	1.11	0.83
Cyclopentene	1.00	1.00
cis-1,3-Pentadiene	0.95	0.78

Relative volatilities for these compounds in the presence of acetonitrile were determined using a two-plate distillation apparatus with a 3:1 volume mixture of acetonitrile and piperylene concentrate. Pot and head samples were analyzed by gas chromatography to determine component concentrations. The relative volatilities were then calculated as

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j}$$

where i and j again refer to the more and less volatile components respectively; x_i corresponds to the mole percent of i in the liquid phase (pot); and y_i refers to the mole percent of i in the vapor phase (head). Since the equipment utilized for determination of these α_{ij} values contained two theoretical plates, the value for each α_{ij} corresponding to the separation achieved by a single plate was obtained by the Fenske equation[3,13]:

$$\mathrm{Nm} = \frac{\log \frac{y_i}{y_j} \cdot \frac{x_j}{x_i}}{\log \alpha_{ij}} \quad .$$

In this equation, α_{ij} obtained for two plates corresponds to the product in the numerator, Nm designates the minimum number of plates necessary for the separation (in this case, Nm = 2) and α_{ij} in the denominator is the relative volatility of i to j, the light to heavy component.

Extractive Distillation As A Separation Technique

Theory of extractive distillation has been treated extensively in the literature[12,14-32].

Since piperylene concentrate is a mixture of compounds with similar boiling points (Table II), a separation by simple fractionation is impossible. By adding a solvent to the mixture which changes the relative volatilities of the major components present, separation becomes feasible by extractive distillation. Recalling relative volatility,

$$\alpha_{ij} = S_{ij} \frac{P_i^\circ}{P_j^\circ} ,$$

the effectiveness of a solvent is determined by its ability to alter the selectivity, S_{ij}, because the vapor pressure of a pure compound is a function of temperature, total pressure, and the heat of vaporization of the compound. The further S_{ij} deviates from unity the more effective is the solvent for separating components i and j.

In extractive distillation operations liquid solvent is fed to the distillation column at the top of the column and flows downward, establishing an equilibrium with the condensed distillate on each plate in the column. The solvent has a preferential affinity for one or more components in the mixture and therefore enhances the relative volatility of the other(s).

A solvent may affect the components of a mixture of hydrocarbons by either physical or chemical interactions, or by a combination of the two. A physical interaction is predominant when there is a difference of five percent or more in the molar volumes of the components to be separated. In this instance, solvents with a high polar cohesive energy tend to give better separation. Polar cohesive energy is a measure of the ability of a polar molecule to induce an energy of attraction in a non-polar molecule[25]. The larger the difference in molar volumes, the better the separation; the higher the polar cohesive energy of the solvent, the better the separation. Intermolecular forces are predominantly dispersion and dipole-induced dipole forces between the components in the hydrocarbon mixture to be separated and the polar solvent.

When the molar volumes of the compounds to be separated are equal or very nearly equal, chemical effects must predominate. These interactions depend primarily on formation of loosely-bound aggregates as a result of Lewis acid-base interactions and solvation effects. Hydrocarbons, especially olefins and diolefins, tend to be electron donors and therefore chemical effects contribute to solvent-hydrocarbon interactions[27].

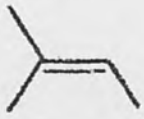
Based on literature values of densities[33], the difference in molar volumes of liquids at 20°C is 5.1% between 2-methyl-2-butene and cyclopentene and 12.5% between 1,3-pentadiene and cyclopentene with cyclopentene having the smallest molar volume of the three

compounds. This indicates a contribution by physical interaction between the hydrocarbons and a polar solvent. In most cases, the physical effects are more pronounced than the chemical effects[27].

Solvent Selection

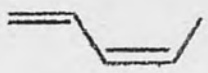
Some of the ideal characteristics of solvents to be considered for extractive distillations include low cost, low toxicity, high stability, low viscosity, non-corrosiveness, a boiling point 50 - 100°C above that of the mixture to be separated, absence of azeotrope formation with components to be separated, ease of separation from bottoms product(s), and, most importantly, an ability to change the relative volatility of the components in the mixture to be separated[12,22,31]. For the specific separation with which this project deals, in order to have a marked effect on relative volatilities, a solvent should be electron withdrawing and have easy access (sterically) to the withdrawing portion of the molecule. This will allow interactions between solvent molecules and the π-electrons in the compounds to be separated.

Comparing the structures of the four major components

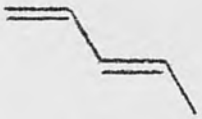


2-methyl-2-butene

cyclopentene



cis-1,3-pentadiene



trans-1,3-pentadiene

one can see how π electrons involved in the C=C bonds are in different environments in each molecule. As expected, the diolefins were found to interact with electron withdrawing solvents more strongly than the olefin compounds. Because the cis isomer is less sterically hindered, its interaction with the solvent is stronger than that of the trans isomer.

An additional contribution to the enhanced interaction between solvent and the major components in piperylene concentrate results from hyperconjugation. When a C-H bond is located alpha to a π bond, the σ electrons of the C-H bond may be involved in a resonance structure; this electron delocalization is termed hyperconjugation[34]. Cyclopentene, 2-methyl-2-butene and the 1,3-pentadienes have these C-H bonds present in an alpha position and therefore have additional abilities to interact with electron withdrawing solvent molecules, since the delocalized electrons are more mobile.

Compared to cyclopentene, 2-methyl-2-butene is slightly more volatile in the presence of solvent, due to steric hindrance around the C=C bond in 2-methyl-2-butene.

To simplify comparison of effectiveness of various solvents,

the relative volatility of cyclopentene to the cis isomer was chosen since there was a significant difference in their behavior with polar solvents. The cis isomer was rapidly determined to be the least volatile major component in piperylene concentrate because of its ability to interact with solvent molecules, and was chosen as the heavier key. Since 2-methyl-2-butene was present in a relatively small concentration (Table I), it was not selected as being the lighter key indicative of the effectiveness of the separation. Cyclopentene was chosen rather than trans-1,3-pentadiene as the lighter key because all solvents investigated reversed the relative volatility of these two compounds (Table V), making cyclopentene more volatile than both 1,3-pentadienes. This selection guaranteed all α values involving 1,3-pentadienes to have positive deviations from unity, i.e., values greater than one.

Table VI summarizes some of the properties of the solvents investigated. Of those listed, acetonitrile is the solvent of choice for several reasons other than selectivity. First, the low viscosity indicates a small amount of work required for pumping and a relative ease with which it can flow through a plate column. Of the solvents for which allowable limits in the air were available, acetonitrile has the highest limit indicating it is less toxic than the others. In addition to these desirable properties, the relative cost of acetonitrile is considerably less than that of the alternative solvents, all of which are less effective. One point to be

TABLE VI

SOLVENT PROPERTIES

SOLVENT	mp (°C)[a]	bp (°C)[a]	M_r[a]	DENSITY (g per ml)[a]	TOXICITY[a,b]	VISCOSITY (°C, cp)[a]	COST ($ per kg)[c]	SUPPLIER	SEPARATION FACTOR[d]
Acetonitrile	-45.72	81.6	41.05	0.7857	40	25,0.345	5.90	Burdick & Jackson	1.45
Benzonitrile	-13	190.7	103.13	1.0102	—	25, 1.24	10.00[e]	J. T. Baker	1.15
N,N-Dimethyl-formamide	-60.48	149-56	73.09	0.9487	skin-10	25,0.802[f]	9.35	Aldrich	1.24
Dimethyl Sulfoxide	18.45	189	78.13	1.1014	—	——	8.40	Fisher	1.23
Ethylene-diamine	8.5	116.5	60.11	0.8994	10	25, 0.0154[f]	14.70	Matheson, Cole-man & Bell	1.12
Nitrobenzene	5.7	210.8	123.11	1.2037	skin-1	20, 2.03	7.00	Fisher	1.13
Propionitrile	-92.89	97.35	55.08	0.7818	—	——	86.50[h]	Matheson, Cole-man & Bell	1.16
Sulfolane	28[h]	285[h]	120.17	——	—	——	28.50[e]	Phillips Petroleum	1.20

[a] Reference 33 (boiling points at 760 mm)
[b] Allowable human exposire in air, ppm vapor by volume at 25°C, 760 mm
[c] Reference 36, based on 1 kg purchase, except as noted
[d] For cyclopentene/cis-1,3-pentadiene, based on experimental α (Table VIII) and volatilities (Table V)
[e] Based on 0.5 kg purchase
[f] Reference 35
[g] Based on 0.1 kg purchase
[h] Reference 3

stressed is that the costs given are based on purchase prices for small quantities of material and should be viewed only on a relative basis.

According to the literature[37,38], very few azeotropes are formed with acetonitrile (water, carbon tetrachloride, and n-pentane form azeotropes), all of which distill at temperatures considerably higher than the major components of piperylene concentrate.

The boiling point of acetonitrile at 81.6°C[33] is about 40°C above the boiling points of the components to be separated. This is a smaller difference than the recommended 50 - 100°C boiling point difference. This can be used advantageously in that it allows the solvent to be recovered in pure form by distillation at a lower cost than a solvent which has a higher boiling point.

Acetonitrile has been used to separate four-carbon paraffins from olefins and to separate butenes from butadienes. Furfural has also been investigated as a solvent for this separation but acetonitrile was preferred because of its low molecular weight and density. This allows equipment sizes and utility usages to be less for increased economic gains[3].

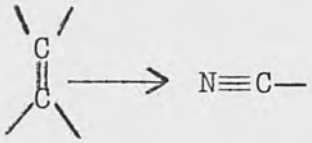
Solvents suitable for separation of paraffin/olefin pairs are also usually suitable for olefin/diolefin separations. Gerster and co-workers[19] have determined selectivities (γ_i/γ_j) for the pentane/1-pentene separation by extractive distillation for several solvents. From their results the solvents dealt with here, in order

of increasing selectivity are propionitrile, ethylenediamine, N,N-dimethylformamide, and acetonitrile. Solvents which exceeded acetonitrile's selectivity, in order of increasing selectivity, were β-chloropropionitrile, γ-butyrolactone, and nitromethane. Gerster and co-workers concluded that high selectivity of a solvent was directly proportional to the degree of deviation from ideality of the solution of solvent and components to be separated. Also, solvents which are capable of hydrogen bonding were found to have a lower selectivity than those which cannot form hydrogen bonds. They concluded that no particular functional group was more effective than others; and no particular spatial arrangement of functional group(s) was more effective.

Tassios[27] has also investigated the pentane/1-pentene system for separation by extractive distillation and has ranked the same four solvents as Gerster but found the order of ethylenediamine and N,N-dimethylformamide to be reversed. He has also listed γ-butyrolactone and nitromethane as superior to acetonitrile for this separation.

For extractive distillation of hydrocarbons in general Prausnitz and Anderson[25] have determined some guidelines which seem applicable, including small molecular size and high polarity of solvent, particularly that an ideal solvent should have electron accepting capabilities to withdraw electrons from the π bonds in the olefins. Thus, the nitrogen atom in the nitrile group withdraws

electrons from the C=C bond in the olefin to form a complex[25].



Electron donor-acceptor interaction is a Lewis acid-base interaction and is the basis of the chemical effect of the solvent.

Weimer and Prausnitz[29] have reported data on polar solvents used in hydrocarbon systems including polar and non-polar solubility parameters. Their conclusions were that selectivity depends primarily on the solvent's polar cohesive energy and on its molecular size. Solvent selectivity is good when the polar cohesive energy is large and the molecular size is small.

N,N-dimethylformamide, herein determined to give the second most effective separation efficiency, has been utilized in the extractive distillation of 2-methyl-1,3-butadiene (known commonly as isoprene) from 2-methyl-2-butene with good success[26]. Japan's GPB process also uses N,N-dimethylformamide in an extractive distillation to separate 1,3-butadiene from the four-carbon hydrocarbon by-product of ethylene production[39,40]. This solvent has disadvantages in that it is less effective, more dense, has a higher molecular weight, is more toxic, more viscous, and more expensive than acetonitrile.

The third most effective solvent investigated was dimethyl sulfoxide which is slightly cheaper than N,N-dimethylformamide.

Its molecular weight is slightly higher as is its density. Viscosity and toxicity data were not available.

For industrial applications, chemicals which remain liquid over a wide range of temperatures are preferred for ease of handling independent of climate or weather conditions. Dimethyl sulfoxide and sulfolane both have melting points near room temperature which is a disadvantage. Very little literature information is available for sulfolane, a relatively new industrial chemical made from butadiene. Sulfolane is being used by Shell Oil Company in extractive distillation of aromatics from catalytic reformates, and in the Sulfinol process with alkanolamines to purify hydrogen[14]. For the extractive distillation of piperylene concentrate based on the relative cost as shown in Table VI, sulfolane would not seem to be very economical, although it was determined to be the fourth most effective solvent investigated.

The remaining four solvents investigated do not warrant further discussion or experimentation as their effectiveness was negligible for the problem at hand and each has disadvantages as shown in Table VI.

RESULTS

The results of the 19 best runs, based on the separation of cyclopentene from cis-1,3-pentadiene are summarized in Table VII and Table VIII. These results appear in order of decreasing effectiveness in the cyclopentene/cis isomer separation.

The mode of distillation refers only to the method of solvent introduction. Batch runs were performed by adding measured amounts of both solvent and piperylene concentrate into the still pot prior to heating; continuous refers to an initial charging of piperylene concentrate to the still pot and continuously pumping solvent into the top of the distillation column during the distillation.

The α values reported on Table VIII correspond to the separation achieved by a single theoretical plate for comparison of runs on the small column to runs on the large column. These α's were calculated by substituting Nm=8 for the small column and Nm=12 for the large column in the Fenske equation; the numerator was obtained by the concentrations of head and pot samples analyzed by gas chromatography. The Fenske equation was then solved for α_{ij}, the term in the denominator which is reported in Table VIII.

TABLE VII

DISTILLATION OPERATING CONDITIONS

RUN	SOLVENT	MODE[a]	SOLVENT FLOW RATE(ml per min)	DISTILLATE FLOW RATE(ml per min)	SOLVENT TO DISTILLATE FLOW RATIO	SOLVENT FEED TEMPERATURE(°C)
A	Acetonitrile	C	3.29	0.324	10.0:1	60
B	Acetonitrile	C	1.15	0.491	2.3:1	63
C	Acetonitrile	C[b]	0.85	0.599	1.4:1	55
D	Acetonitrile	C	2.41	0.466	5.2:1	75
E	Acetonitrile	B	——	0.348	4.0:1	—
F	Acetonitrile/Water (90%/10%)	C	1.00	0.426	2.4:1	45
G	Acetonitrile	C	1.97	0.615	3.2:1	60
H	Acetonitrile	C	1.95	0.263	7.4:1	55
I	N,N-Dimethylformamide	C	1.32	0.467	2.8:1	85
J	Dimethyl Sulfoxide	C	2.15	1.260	1.7:1	100
K	Acetonitrile	C	1.31	0.243	5.4:1	55
L	Acetonitrile	B	——	0.794	4.0:1	—
M	Dimethyl Sulfoxide	C	1.91	0.765	2.5:1	70
N	N,N-Dimethylformamide	B	——	0.349	4.0:1	—
O	Sulfolane	C	1.72	0.795	4.0:1	90
P	Propionitrile	B	——	0.187	4.0:1	—
Q	Benzonitrile	B	——	0.210	4.0:1	—
R	Nitrobenzene	C	1.42	1.53	1.0:1	45
S	Ethylenediamine	B	——	0.263	4.0:1	—

[a] B = Batch; C = Continuous

[b] Reflux Ratio at 4:1; Remainder at 1:1

TABLE VIII

EXPERIMENTAL ALPHA VALUES

RUN	2-METHYL-2-BUTENE / CYCLOPENTENE	CYCLOPENTENE / trans-1,3-PENTADIENE	CYCLOPENTENE / cis-1,3-PENTADIENE	trans-1,3-PENTADIENE / cis-1,3-PENTADIENE	CYCLOPENTENE / TOTAL 1,3-PENTADIENE
A	1.267	1.321	1.375	1.094	1.326
B	1.161	1.183	1.326	1.067	1.207
C	1.283	1.215	1.316	1.083	1.242
D	1.149	1.212	1.293	1.067	1.235
E	1.214	1.158	1.292	1.115	1.205
F	1.157	1.178	1.290	1.095	1.212
G	1.159	1.199	1.290	1.076	1.227
H	1.140	1.186	1.276	1.076	1.216
I	1.221	1.109	1.178	1.069	1.127
J	1.241	1.062	1.167	1.098	1.093
K	1.347	1.073	1.165	1.107	1.108
L	1.189	1.089	1.163	1.086	1.109
M	1.269	1.058	1.162	1.102	1.086
N	1.240	0.981	1.146	1.168	1.035
O	———	1.059	1.137	1.085	1.086
P	1.215	1.042	1.104	1.083	1.060
Q	1.223	0.952	1.088	1.122	0.978
R	———	1.010	1.076	1.065	1.034
S	1.430	0.946	1.061	1.106	0.985

DISCUSSION AND CONCLUSIONS

As can be seen by the results given in Tables VII, VIII, IX, and X for piperylene concentrate separation by extractive distillation, acetonitrile's effectiveness was much better than the other solvents investigated, especially for the separation of cyclopentene from the 1,3-pentadienes.

Optimum conditions for good separation of cyclopentene from cis-1,3-pentadiene included high rate of distillate flow through the system, high ratio of acetonitrile flow to distillate flow, and relatively high temperature of acetonitrile (60-65°C) feed to the column which resulted in an increased rate of flow of distillate. Both the presence of a ten percent by volume of water in the acetonitrile solvent and an increase in reflux ratio from 1:1 to 4:1 produced an increase in the separation of these two components, with the increase in reflux ratio having the greater effect.

For the separation of cyclopentene from trans-1,3-pentadiene, high temperature of solvent feed (about 60°C) and the resultant high distillate flow rate improved acetonitrile's effectiveness. An increase in solvent to distillate flow ratio did not necessarily increase the separation nor did the presence of water in the acetonitrile solvent. An increase in the reflux ratio, however, had a marked increase in the separation of cyclopentene from the trans

TABLE IX

DISTILLATION RUNS IN ORDER OF DECREASING EFFECTIVENESS FOR SEPARATION OF COMPONENT PAIRS

2-METHYL-2-BUTENE / CYCLOPENTENE	CYCLOPENTENE / *trans*-1,3-PENTADIENE	CYCLOPENTENE / *cis*-1,3-PENTADIENE	*trans*-1,3-PENTADIENE / *cis*-1,3-PENTADIENE	CYCLOPENTENE / TOTAL 1,3-PENTADIENE
S	A	A	N	A
K	C	B	Q	C
C	D	C	E	D
M	G	D	K	G
A	H	E	S	H
J	B	F	M	F
N	F	G	J	B
Q	E	H	F	E
I	I	I	A	I
P	L	J	L	L
E	K	K	O	J
L	J	L	P	K
B	O	M	C	O
G	M	N	H	M
F	P	O	G	P
D	R	P	I	N
H	N	Q	D	R
	Q	R	B	S
	S	S	R	Q

TABLE X

INVESTIGATED SOLVENTS IN ORDER OF DECREASING EFFECTIVENESS FOR SEPARATION OF COMPONENT PAIRS

2-METHYL-2-BUTENE / CYCLOPENTENE	CYCLOPENTENE / *trans*-1,3-PENTADIENE	CYCLOPENTENE / *cis*-1,3-PENTADIENE	*trans*-1,3-PENTADIENE / *cis*-1,3-PENTADIENE	CYCLOPENTENE / TOTAL 1,3-PENTADIENE
Ethylenediamine	Acetonitrile	Acetonitrile	N,N-Dimethyl-formamide	Acetonitrile
Acetonitrile	Acetonitrile/ Water(90%/10%)	Acetonitrile/ Water(90%/10%)	Benzonitrile	Acetonitrile/ Water(90%/10%)
Dimethyl Sulfoxide	N,N-Dimethyl-formamide	N,N-Dimethyl-formamide	Acetonitrile	N,N-Dimethyl-formamide
N,N-Dimethyl-formamide	Dimethyl Sulfoxide	Dimethyl Sulfoxide	Ethylenediamine	Dimethyl Sulfoxide
Benzonitrile	Sulfolane	Sulfolane	Dimethyl Sulfoxide	Sulfolane
Propionitrile	Propionitrile	Propionitrile	Acetonitrile/ Water(90%/10%)	Propionitrile
Acetonitrile/ Water(90%/10%)	Nitrobenzene	Benzonitrile	Sulfolane	Nitrobenzene
	Benzonitrile	Nitrobenzene	Propionitrile	Ethylenediamine
	Ethylenediamine	Ethylenediamine	Nitrobenzene	Benzonitrile

isomer.

In the evaluation of solvents by decreasing effectiveness (Table IX) it can be seen that the cyclopentene/1,3-pentadiene separations are all similar. More specifically, solvent selectivity for cyclopentene separation from the cis isomer is of the same order as the separation of cyclopentene from the cis and trans isomers, with the reversal of the order of appearance of ethylenediamine and benzonitrile. The only point of difference between the separation of cyclopentene from the cis isomer and the separation of cyclopentene from the trans isomer is in the reversal of the order of appearance of nitrobenzene and benzonitrile. In each of these three separations, the listed reversed orders of appearance involving nitrobenzene, ethylenediamine and benzonitrile are rearrangements of the three least effective solvents of those investigated.

For the separation of cis- from trans-1,3-pentadiene, good results were obtained in batch distillations, indicating the extreme importance of high solvent concentration for good separation of these isomers. Consequently, for continuous results, high acetonitrile to distillate flow ratios with low-temperature solvent feed (55°C and less) gave better results which seemed to be independent of absolute distillate flow rates. The presence of water had a beneficial effect on acetonitrile's effectiveness, more so than an increase in solvent concentration. An increase in reflux ratio had little effect on the capability of acetonitrile for the separation

of the cis isomer from the trans isomer.

As Table X indicates, acetonitrile was not found to give the best cis/trans separation results, but was exceeded by both N,N-dimethylformamide (DMF) and benzonitrile. Results obtained with DMF (α = 1.168) were better than with benzonitrile (α = 1.122). The third-best run (α = 1.115) was with acetonitrile. Optimization of the separation of cis- from trans-1,3-pentadiene should include further investigation of the use of DMF and/or benzonitrile in a subsequent extractive distillation of the mixed product obtained by separation of piperylene concentrate with acetonitrile. Another solvent which should be investigated for this separation is dimethyl sulfoxide.

It has been reported that separation of cis- from trans-1,3-pentadiene has been achieved by complex formation with silver nitrate or silver perchlorate[41]. This separation was not investigated in this project.

The effectiveness of separation of 2-methyl-2-butene from cyclopentene with acetonitrile was exceeded only by ethylenediamine (Table X). Again, the effect of dimethyl sulfoxide warrants further investigation as does N,N-dimethylformamide for the separation of 2-methyl-2-butene from cyclopentene.

Based on the best separation of a given component pair achieved with acetonitrile as solvent, the number of theoretical plates required for separation to obtain 99% pure products was calculated

by using the Fenske equation[13,27]. These results are reported in Table XI along with the required plates for pair separations under the conditions of Run A.

All component pair separations given can be achieved by 33 theoretical plates with the exception of cis- from trans-1,3-pentadiene which would require 84 plates, based on the maximum separation achieved in this work. Comparing the results from all separations at the conditions of Run A, 39 theoretical plates are required for the 2-methyl-2-butene separation from cyclopentene and the plate requirements for cis/trans separation is increased to 103. From this calculation, the separation of piperylene concentrate by extractive distillation would probably be achieved most economically by removing the cis and trans isomers as a mixture and carrying out their separation by other means, perhaps with an alternative solvent (i.e. N,N-dimethylformamide, benzonitrile, dimethyl sulfoxide, or another solvent).

These results indicate an extractive distillation of piperylene concentrate with acetonitrile solvent under conditions of high solvent concentration (10:1 solvent:distillate) fed at a moderate to high temperature (60°C) for recovery of 99% 2-methyl-2-butene, 99% cyclopentene, and cis- and trans-1,3-pentadiene (mixed) products is feasible in a column containing 39 theoretical plates.

TABLE XI

DISTILLATION CONDITIONS AND NECESSARY PLATES FOR COMPONENT PAIR SEPARATION

PAIR TO SEPARATE	α_{max}	RUN	SOLVENT TO DISTILLATE RATIO	SOLVENT TEMPERATURE(°C)	MINIMUM NUMBER OF PLATES
2-Methyl-2-butene/Cyclopentene	1.347	K	5.4:1	55	31
2-Methyl-2-butene/Cyclopentene	1.267	A	10.0:1	60	39
Cyclopentene/trans-1,3-Pentadiene	1.321	A	10.0:1	60	33
Cyclopentene/cis-1,3-Pentadiene	1.375	A	10.0:1	60	29
trans-1,3-Pentadiene/cis-1,3-Pentadiene	1.115	E	4.0:1	—	84
trans-1,3-Pentadiene/cis-1,3-Pentadiene	1.094	A	10.0:1	60	103
Cyclopentene/Total 1,3-Pentadiene	1.326	A	10.0:1	60	33

RECOMMENDATIONS

Based on the results obtained in this study, the following recommendations are made:

1. For extractive distillation of piperylene concentrate to obtain 99% pure 2-methyl-2-butene, 99% pure cyclopentene, and a mixture of cis- and trans-1,3-pentadiene, acetonitrile is a suitable solvent for use in a tower which contains 39 theoretical plates in conjunction with a "tailing" section to remove solvent entrained in the distillate.
2. Operating conditions for the separation in recommendation one should be as follows: piperylene concentrate should be charged on a batch basis to the distillation tower; flow ratio of acetonitrile to distillate should be 10:1; and acetonitrile feed to the column should be heated to approximately 60°C prior to introduction to the system.
3. Reduction of plate requirements may be possible by further investigation of acetonitrile-water mixed solvent behavior.
4. Reduction of plate requirements may be possible by further investigation of changes in reflux ratio.
5. Additional solvents which should be screened for possible greater selectivity include β-chloropropionitrile, γ-butyrolactone, and nitromethane.

6. The use of ethylenediamine, dimethyl sulfoxide, and N,N-dimethylformamide should be investigated for separation of 2-methyl-2-butene from piperylene concentrate prior to cyclopentene separation by acetonitrile extractive distillation.
7. Further 1,3-pentadiene isomer separation may be feasible (following acetonitrile extractive distillation) by using a solvent such as N,N-dimethylformamide, benzonitrile, or dimethyl sulfoxide in a subsequent extractive distillation.
8. Conditions for operation with continuous piperylene feed to the tower (as opposed to a batch charge) should be established for large scale industrial applications.

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